

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**APPLICATION FOR LETTERS PATENT**

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**Semiconductor Processing Methods Of Chemical  
Vapor Depositing SiO<sub>2</sub> On A Substrate**

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**INVENTOR**

**Klaus F. Schuegraf**

ATTORNEY'S DOCKET NO. MI22-482

**EL169836626**

**EM189770036**

*[Handwritten Signature]*

TECHNICAL FIELD

This invention relates to semiconductor processing methods of chemical vapor depositing SiO<sub>2</sub> on a substrate.

BACKGROUND OF THE INVENTION

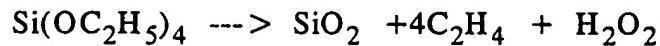
Chemical vapor deposited (CVD) SiO<sub>2</sub> films and their binary and ternary silicates find wide use in VLSI processing. These materials find use as insulators between polysilicon and metal layers, between metal layers in multilevel metal systems, as diffusion sources, as diffusion and implantation masks, as capping layers to prevent outdiffusion, and as final passivation layers.

The manner in which a thin film covers or conforms to the underlying features on a substrate is an important characteristic in semiconductor processing. Conformal coverage refers to coverage in which equal film thickness exists over all substrate topography regardless of its slope, i.e. vertical and horizontal substrate surfaces are coated with equal film thickness.

One manner of effecting the deposition of SiO<sub>2</sub> on a substrate is through pyrolysis of an organic silicon precursor in a CVD reactor to form SiO<sub>2</sub>. A typical organic silicon precursor is tetraethoxysilane or TEOS which is represented by the chemical formula Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. A typical reactor used to effect the pyrolysis of organic silicon precursors is a low pressure CVD reactor or LPCVD reactor. LPCVD

reactors include both hot wall and cold wall reactors. In hot wall reactors, wafers can be heated utilizing radiant heat supplied from resistance-heated coils. In cold wall reactors, wafers can be heated utilizing infrared lamps or rf induction.

LPCVD reactors are typically operated at pressures of around 0.25-2.0 Torr and temperatures of around 550° C to 800° C, although such parameters may vary depending on a number of different conditions including the particular types of reactants used. The stoichiometry of decomposition of TEOS within an LPCVD reactor may be simplistically written as:



Typically, however, intermediates are formed in the above reaction which include di-ethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_3\text{OH}$ ) and tri-ethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_2(\text{OH})_2$ ). Further, other reaction by-products are formed.

One problem facing the semiconductor wafer processor is achieving adequate and conformal step coverage of deposited  $\text{SiO}_2$  into very deep and narrow contact openings or other so-called high aspect ratio topographies. One such substrate surface topography is depicted in Figs. 1 and 2 and designated generally by reference numeral 10. Topography 10 is defined by a deep trench 12 into which an  $\text{SiO}_2$  layer 14 has been deposited as by CVD of a suitable organic silicon precursor such as TEOS.

Fig. 1 illustrates a situation in which adequate conformality has been achieved as evidenced by the uniformity or substantial uniformity in thickness of layer 14 over the substrate surface, and particularly within trench 12. Fig. 2 illustrates a situation in which inadequate conformality has resulted in non-uniformity in the thickness of layer 14, particularly at and near the bottom of trench 12. Such is an undesirable condition.

One source of inadequate conformality of  $\text{SiO}_2$  on a substrate surface is premature formation of undesirable intermediates which react to form  $\text{SiO}_2$  at higher topographical elevations on a substrate surface. Consequently, such intermediates never reach the bottom of a particular substrate feature, such as trench 12 of Fig. 2, so that lesser degrees of  $\text{SiO}_2$  are formed thereon.

One method to improve step coverage has been to increase pressures in the CVD reactor. By doing so, the partial pressure of the organic silicon precursor, such as TEOS, is increased, while the partial pressure of the intermediates is not. The increase in organic silicon precursor partial pressure results in improved step coverage because the precursor has a more favorable sticking coefficient as compared with the intermediates.

Another attempt to increase step coverage has been to introduce ethylene ( $\text{C}_2\text{H}_4$ ) into the reactor with the precursor to inhibit the premature formation of intermediates. Unfortunately, great success has

1       not been achieved due to significant degradation of deposition rates  
2       stemming from competitive absorption relative to the substrate surface  
3       as between the ethylene and the precursor.

4       This invention grew out of the need to provide improved step  
5       coverage of LPCVD SiO<sub>2</sub> over high aspect ratio substrate topography.  
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7       SUMMARY OF THE INVENTION

8       The invention provides semiconductor processing methods of  
9       depositing SiO<sub>2</sub> on a substrate.

10      In a preferred aspect, the invention provides methods of reducing  
11     the formation of undesired reaction intermediates in a chemical vapor  
12     deposition (CVD) decomposition reaction. In one implementation, the  
13     method is performed by feeding at least one of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> into  
14     a reactor with an organic silicon precursor. For example, in one  
15     exemplary implementation, such components are, in gaseous form, fed  
16     separately into the reactor. In another exemplary implementation, such  
17     components are combined in liquid form prior to introduction into the  
18     reactor, and thereafter rendered into a gaseous form for provision into  
19     the reactor. The invention can be practiced with or in both hot wall  
20     and cold wall CVD systems.

1      **BRIEF DESCRIPTION OF THE DRAWINGS**

2      Preferred embodiments of the invention are described below with  
3      reference to the following accompanying drawings.

4      Fig. 1 illustrates a so-called high aspect ratio semiconductor  
5      topography in the form of a trench into which silicon dioxide has been  
6      deposited achieving adequate conformal coverage.

7      Fig. 2 illustrates a high aspect ratio semiconductor topography  
8      similar to Fig. 1, only one in which inadequate conformal coverage has  
9      been achieved.

10     Fig. 3 is a schematic diagram of a chemical vapor deposition  
11    system which may be used in conjunction with one preferred aspect of  
12    the invention.

13     Fig. 4 is a schematic diagram of a chemical vapor deposition  
14    system which may be used in conjunction with another preferred aspect  
15    of the invention.

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1            **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

2            This disclosure of the invention is submitted in furtherance of the  
3            constitutional purposes of the U.S. Patent Laws "to promote the  
4            progress of science and useful arts" (Article 1, Section 8).

5            In accordance with one aspect of the invention, a semiconductor  
6            processing method of chemical vapor depositing SiO<sub>2</sub> on a substrate  
7            comprises:

8            placing a substrate within a chemical vapor deposition reactor;

9            feeding an organic silicon precursor into the chemical vapor  
10          deposition reactor having the substrate positioned therein under  
11          conditions effective to decompose the precursor into SiO<sub>2</sub> which deposits  
12          on the substrate and into a gaseous oxide of hydrogen; and

13          feeding an additional quantity of the gaseous oxide of hydrogen  
14          into the reactor while feeding the organic silicon precursor to the  
15          reactor.

16          In accordance with another aspect of the invention, a  
17          semiconductor processing method of reducing the decomposition rate of  
18          an organic silicon precursor in a chemical vapor deposition process of  
19          depositing SiO<sub>2</sub> on a substrate within a chemical vapor deposition  
20          reactor comprises feeding at least one of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> into the  
21          reactor while feeding the organic silicon precursor.

1           In accordance with another aspect of the invention, a  
2 semiconductor processing method of chemical vapor depositing SiO<sub>2</sub> on  
3 a substrate comprises:

4           placing a substrate within a chemical vapor deposition reactor; and  
5           feeding an organic silicon precursor and feeding an oxide of  
6 hydrogen into the chemical vapor deposition reactor having the substrate  
7 positioned therein under conditions effective to deposit an SiO<sub>2</sub> layer  
8 on the substrate.

9           In accordance with another aspect of the invention, a  
10 semiconductor processing method of reducing the formation of undesired  
11 reaction intermediates in a chemical vapor deposition decomposition  
12 reaction of an organic silicon precursor into silicon dioxide within a  
13 chemical vapor deposition reactor comprises feeding at least one of H<sub>2</sub>O  
14 and H<sub>2</sub>O<sub>2</sub> into the reactor with the organic silicon precursor.

15          Figs. 3 and 4 show schematic diagrams of a different chemical  
16 vapor deposition (CVD) systems both of which are designated at 16.  
17 The preferred semiconductor processing methods may be carried out in  
18 either system in accordance with the description below. The system of  
19 Fig. 3 is configured slightly differently from the system of Fig. 4 as will  
20 become apparent below. Preferably, CVD systems 16 are low pressure  
21 chemical vapor deposition (LPCVD) hot wall systems, although other  
22 CVD systems, such as cold wall systems can be used as will become  
23 apparent. The illustrated and preferred hot wall systems 16 include a

1 CVD reactor 18 which is configured to carry out depositions at  
2 temperatures between around 640° C to 900° C, and at pressures  
3 between 100 mTorr to 3 Torr. Various gases can be supplied to  
4 reactor 18 from one or more gas sources or bubblers, such as those  
5 shown at 20. Such gas sources or bubblers typically hold or contain  
6 a liquid mixture which is heated to produce a gas. Such gas from gas  
7 sources 20 enters CVD reactor 18 where exposure to temperature and  
8 pressure conditions effect deposition of a material, preferably SiO<sub>2</sub>, on  
9 a semiconductor or wafer substrate therewithin. More than one gas  
10 source (Fig. 4) may be used. Inside of CVD reactor 18, a  
11 semiconductor wafer holder 22 is provided for holding a plurality of  
12 semiconductor wafers or substrates 24. After suitable deposition has  
13 occurred, gaseous by-products are exhausted, together with unused  
14 reactant and/or diluent gases through exhaust port 26. Reactant gases  
15 may be carried by inert diluent or carrier gases such as H<sub>2</sub>, N<sub>2</sub> or Ar.

16 Fig. 3 shows system 16 configured for carrying out one preferred  
17 semiconductor processing method of chemical vapor depositing SiO<sub>2</sub> on  
18 a substrate. Accordingly, system 16 includes a gas source 28. An  
19 example of a suitable gas source is a bubbler which contains liquid  
20 reactants which are subsequently converted into a gas for provision into  
21 a reactor, such as reactor 18. The illustrated and preferred method  
22 includes placing a substrate or substrates, such as those shown at 24,  
23 within a chemical vapor deposition reactor, such as reactor 18.

1 Reactants which are held in gas source 28 are then heated to produce  
2 a gas which is supplied to reactor 18 for further processing in  
3 accordance this method. One such reactant is a suitable organic silicon  
4 precursor which is preferably tetraethoxysilane or TEOS. Such precursor  
5 is fed into reactor 18 wherein substrate 24 is positioned under  
6 processing conditions, such as the temperature and pressure conditions  
7 mentioned above, which are effective to decompose the precursor into  
8  $\text{SiO}_2$ . Although the preferred methods are described as utilizing TEOS  
9 as the preferred organic silicon precursor, other such organic silicon  
10 precursors may be used. Other precursors include: silane, diethylsilane  
11 (DES), tetramethylcyclo-tetrasiloxane (TMCTS), fluorotriethoxysilane  
12 (FTES), and fluorotrialkoxysilane (FTAS). The  $\text{SiO}_2$  deposits on  
13 substrates 24 and preferably into high-aspect topography features such  
14 as trench 12 in Fig. 1. The organic silicon precursor also decomposes  
15 into a gaseous oxide of hydrogen such as  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ . According  
16 to a preferred aspect of the invented method, another reactant,  
17 preferably either  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$ , is provided in liquid form in gas source  
18 28. Such additional quantity of the oxide of hydrogen is fed into  
19 reactor 18 in gaseous form, while feeding the organic silicon precursor  
20 into the reactor. The presence of the additional quantity of the  
21 gaseous oxide of hydrogen shifts the reaction equilibrium in the  
22 direction of the reactants, thus increasing the partial pressure of the  
23 organic silicon precursor. Such inhibits or reduces premature formation  
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1       of undesirable intermediates which heretofore have reduced the  
2       conformality of the deposition process.

3             Referring still to Fig. 3, quantities of TEOS and the additional  
4       quantity of the oxide of hydrogen, both in liquid form, are mixed  
5       together to form a liquid mixture. The liquid mixture formed thereby  
6       is then converted to a gaseous mixture which is thereafter fed into  
7       reactor 18. By first combining liquid forms of the oxide of hydrogen  
8       and the organic silicon precursor, and then feeding the gaseous mixture  
9       produced thereafter into the reactor, the organic silicon precursor and  
10      the additional gaseous quantity of the oxide of hydrogen are fed into  
11      the reactor together. Preferably, the quantity of organic silicon  
12      precursor, in this example TEOS, in the liquid mixture is greater by  
13      volume than the quantity of the oxide of hydrogen. Even more  
14      preferably, the liquid mixture volume comprises between about 5% to  
15      15% of the oxide of hydrogen. Volumes of the oxide of hydrogen less  
16      than about 5% can be utilized to achieve the above-described  
17      advantages. Volumes of about 0.5% or lower of either of the oxides  
18      of hydrogen may also be utilized. Conversion of the liquid mixture to  
19      the gaseous mixture preferably takes place at bubbler temperatures  
20      between about 65° to 80°C with a preferred temperature of about 75°C.  
21      Thereafter, the gaseous mixture is fed into reactor 18 where it is  
22      reacted to deposit SiO<sub>2</sub> on substrates 24 therewithin.

1       The above described method is one in which the organic silicon  
2 precursor and the oxide of hydrogen are first mixed in liquid form to  
3 form a liquid mixture. The liquid mixture is then subjected to  
4 conditions effective to convert it into a gas which is thereafter fed into  
5 the illustrated and preferred hot wall CVD reactor for subsequent  
6 deposition processing at temperatures between around 640°C to 900°C.  
7 The gaseous mixture is fed into the reactor from a common feed  
8 stream.

9       The above described method can also be employed in cold wall  
10 LPCVD systems under the following preferred pressure, temperature and  
11 other relevant operating conditions. Cold wall deposition conditions or  
12 parameters include pressure conditions of around 10 Torr up to an  
13 upper limit of around 80 Torr. A preferred temperature for cold wall  
14 processing is around 400°C with rf plasma power at 600W. Further, in  
15 accordance with this aspect of the invention, O<sub>2</sub> and He flows  
16 respectively, are at 600 sccm and 775 sccm. The preferred organic  
17 precursor is TEOS which is delivered by liquid injection at 975 sccm.  
18 Additionally, a wafer gap to susceptor is around 230 mils. Under the  
19 above conditions, a resulting SiO<sub>2</sub> deposition rate of around 7000  
20 Angstroms/min is possible.

21      Fig. 4 illustrates schematically a CVD system in which two gas  
22 sources or bubblers 30, 32 are shown. Preferably, one of the gas  
23 sources contains the organic silicon precursor, preferably TEOS, and the

1 other gas source contains the additional quantity of the oxide of  
2 hydrogen, either of H<sub>2</sub>O and/or H<sub>2</sub>O<sub>2</sub>. In such system, reactor 18 is  
3 separately fed with such gaseous reactants. A preferred concentration  
4 of gaseous material provided into reactor 18 comprises less than  
5 about 50% by volume of the H<sub>2</sub>O and/or H<sub>2</sub>O<sub>2</sub>. Even more preferably,  
6 the volume of material injected into the reactor comprises between  
7 about 5% to 15% by volume of the H<sub>2</sub>O and/or H<sub>2</sub>O<sub>2</sub>. Quantities of  
8 H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> less than about 5% of the volume of material injected  
9 into the reactor may be utilized to achieve the above-described  
10 advantages. Volumes of about 0.5% or lower of either of the oxides  
11 of hydrogen can reduce the decomposition rate of the organic silicon  
12 precursor sufficiently to allow CVD depositing of SiO<sub>2</sub> on a silicon  
13 substrate.

14 The above described method is one in which the reactants are  
15 provided in separate bubblers or gas sources, and subjected to  
16 conditions effective to convert each to a separate gas. Each separate  
17 gas is then separately fed into the reactor and exposed to temperature  
18 and pressure conditions effective to deposit an SiO<sub>2</sub> layer on the wafers  
19 or substrates held therewithin. The gaseous mixtures are fed into the  
20 reactor from separate feed streams. As in the first-described method,  
21 the above described method may be utilized in cold wall LPCVD  
22 systems under conditions which are the same as or similar to those  
23 mentioned above.

1        In compliance with the statute, the invention has been described  
2        in language more or less specific as to structural and methodical  
3        features. It is to be understood, however, that the invention is not  
4        limited to the specific features shown and described, since the means  
5        herein disclosed comprise preferred forms of putting the invention into  
6        effect. The invention is, therefore, claimed in any of its forms or  
7        modifications within the proper scope of the appended claims  
8        appropriately interpreted in accordance with the doctrine of equivalents.

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